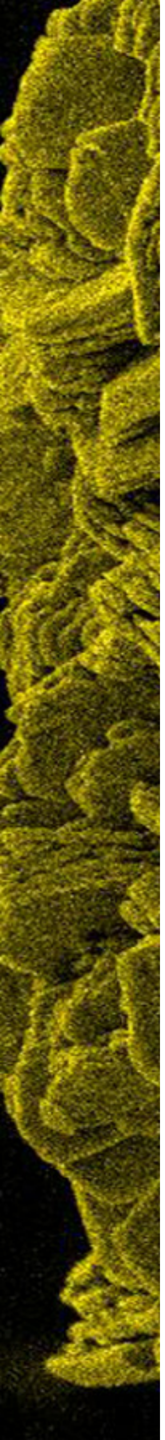

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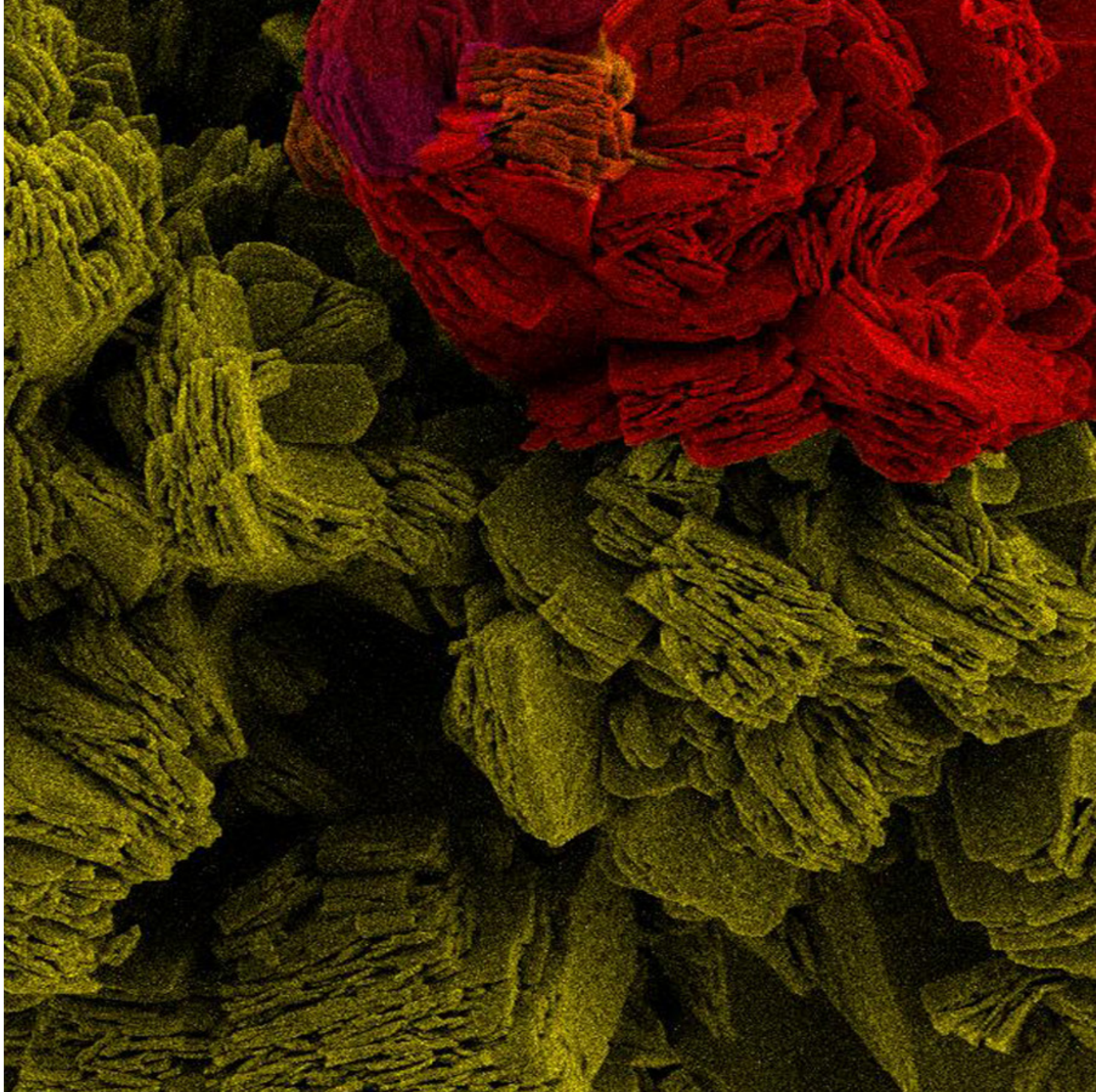
Next-Generation Selective Catalytic Reduction (SCR)-Dosing System Investigation

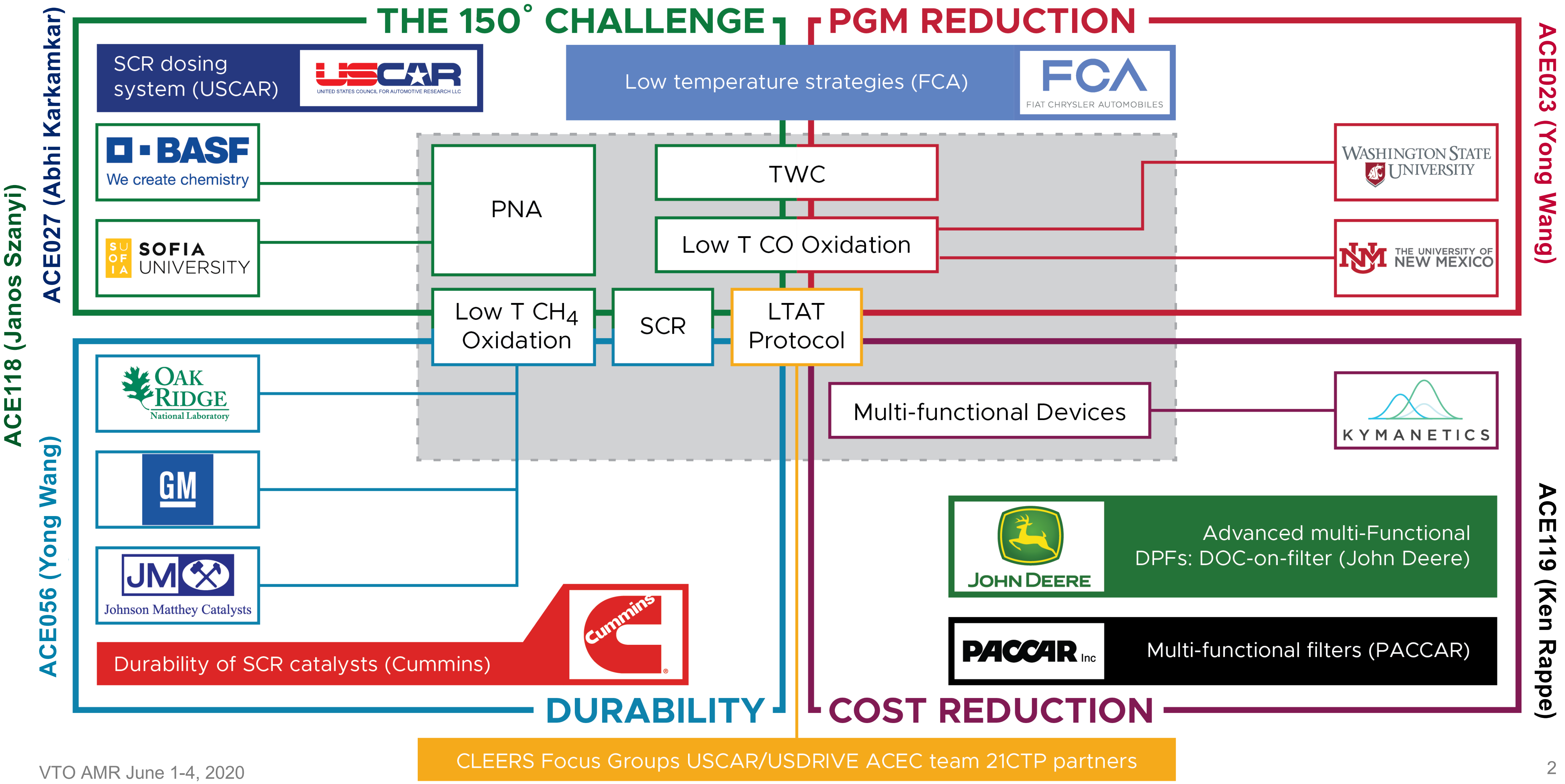
Abhi Karkamkar, Zihao Zhang, Shari Li, Yilin Wang, Yong Wang

June 03, 2020

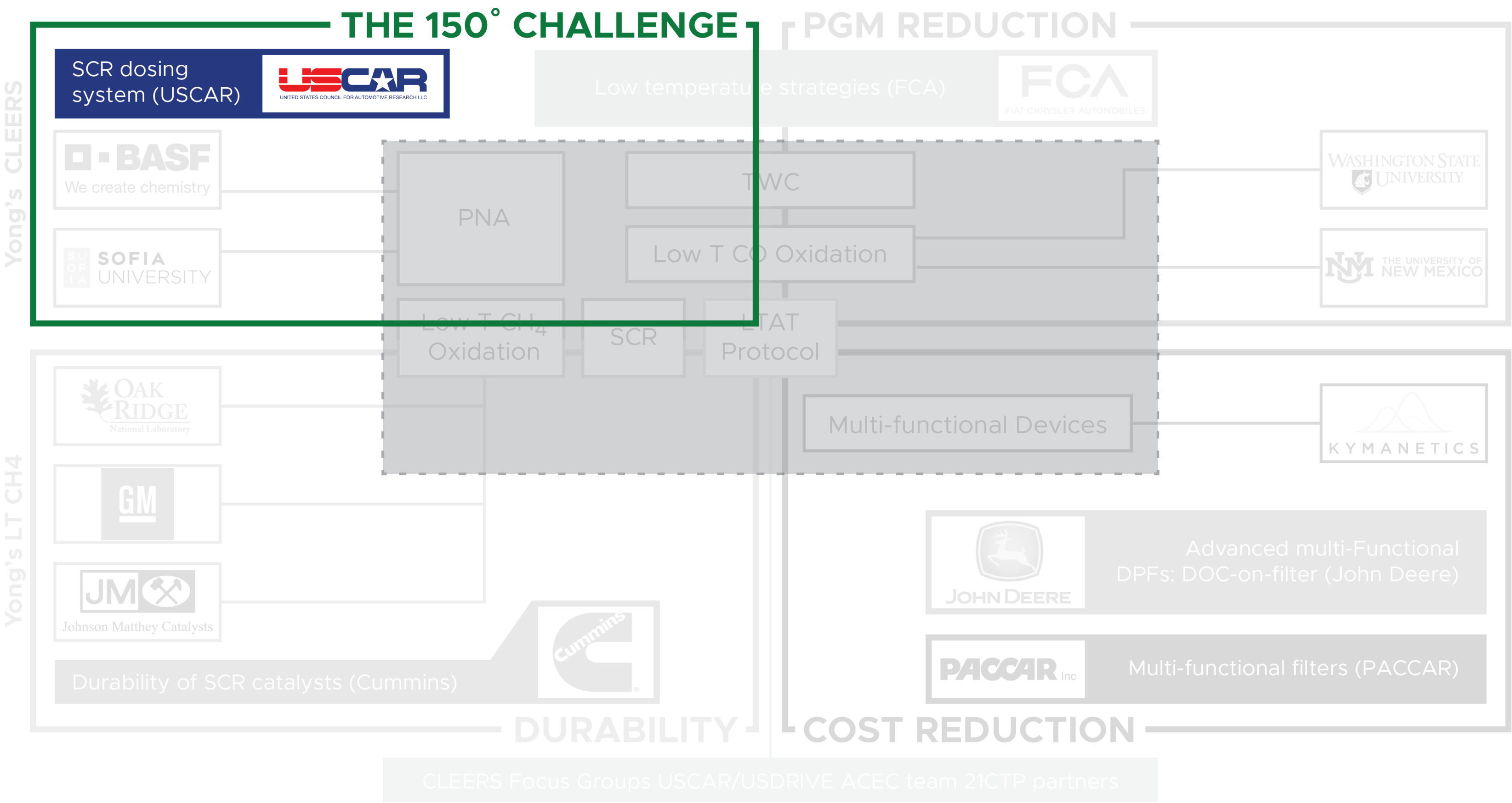
ACE027



PNNL Fundamental and CRADA Projects Address the 150°C Challenge, PGM Reduction, Durability, and Cost - Exemplified by 5 AMR Presentations



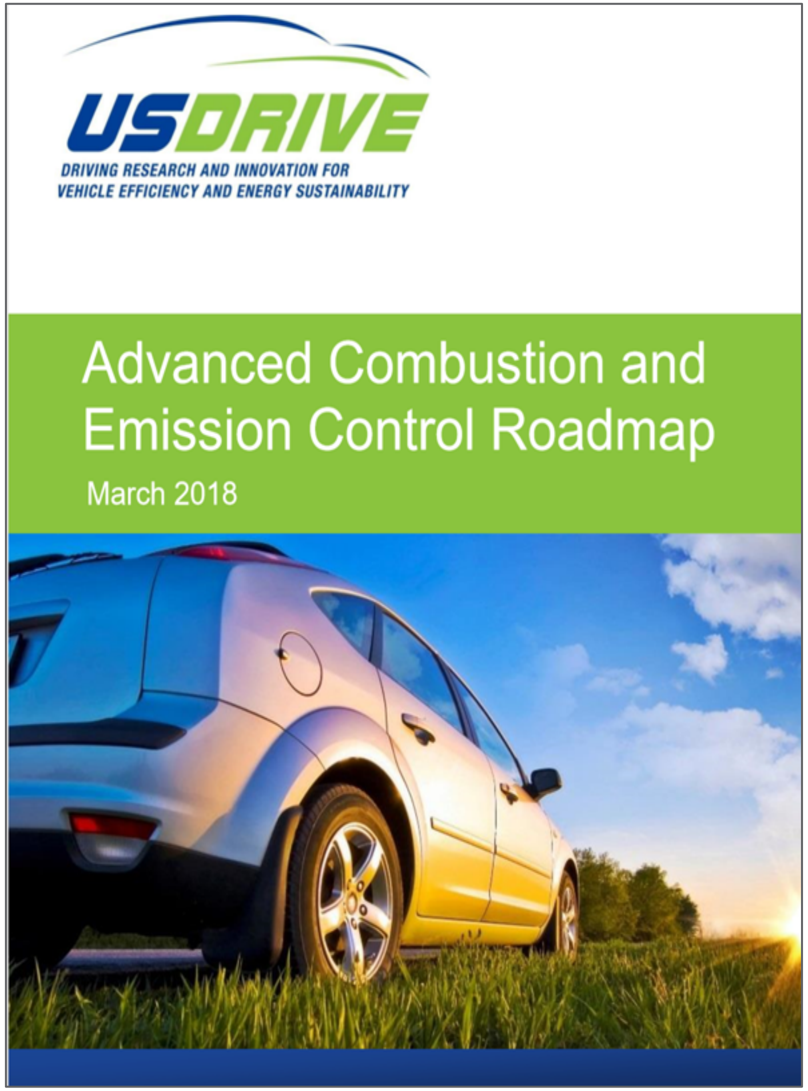
SCR Dosing System for Addressing the 150 ºC Challenge



PNNL objective is the synthesis and evaluation of novel materials for onboard ammonia storage in collaboration with USCAR

Relevance

- Increasing the efficiency of internal combustion engines is limited by the temperature at which the exhaust emission aftertreatment can operate
- Compliance U.S. EPA Tier 3 Bin 30 emission standards
  - Low-temperature emissions aftertreatment
  - Reduced engine-out NOx and particulate emissions
  - Reduced cold start emissions
- New material combinations are needed for lower temperature catalytic performance, increased selectivity to inert species, and optimal storage and delivery of reductant species



Overview

Timeline

- Status:
  - Start date – Oct. 2017
  - End date – Sept. 2020

Budget

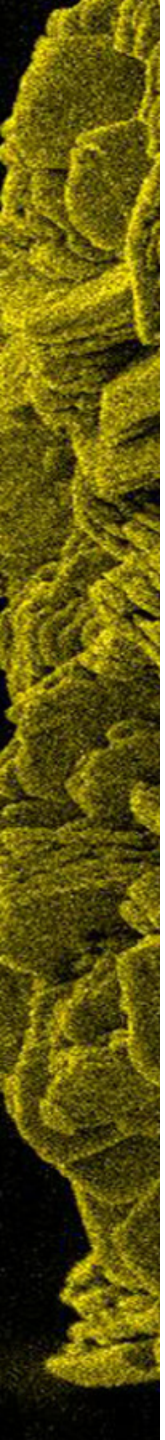
- FY18-FY20 - $600K
- FY20 funding - $200K

Barriers

- Lack of cost-effective emission control
- Durability of emissions control devices
- Effective dissemination of information
- New materials to address the 150 °C

Partners

- U.S. Car SCR working group
- Cummins



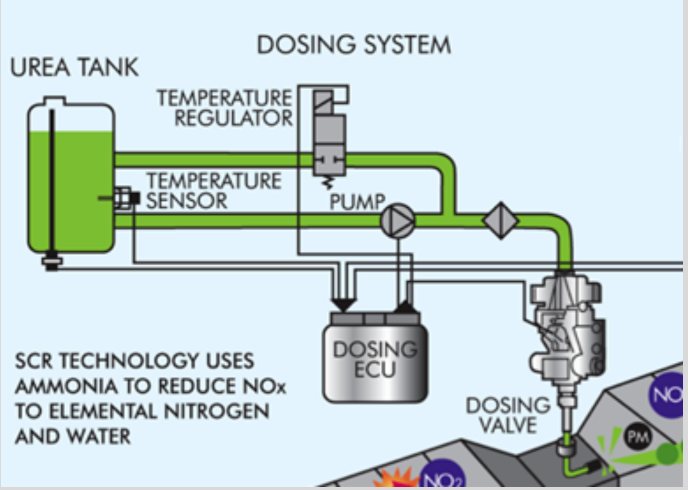
Technical Milestones

	Milestone Description	Date	Status
Milestone	Synthesis and evaluation of at least 5 oxide-based ammonia storage materials	9/30/2019	√
Milestone	Down selection of next generation ammonia storage materials	3/30/2020	√
Milestone	Determine thermodynamic and kinetic parameters	6/30/2020	On track
Milestone	Down select based on thermodynamic/kinetic studies for optimization	9/30/2020	On track

Approach

Alternative on board design

Current on board design



Urea tank

To SCR
T>180 °C

Sorbent
To SCR
T=150-180 °C

Additional NH_3 stored

$MgCl_2(NH_3)_6$

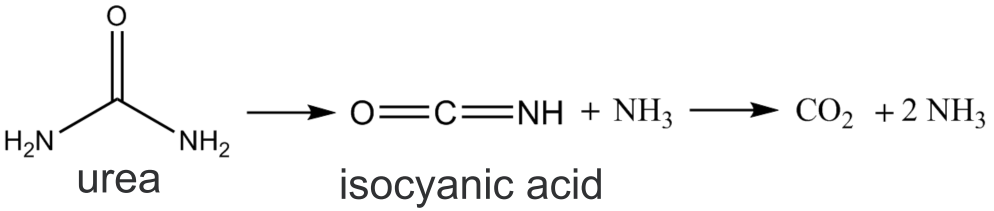
- $2x\ NH_3$ capacity vs DEF
- No deposits
- 125-300 °C dosing range

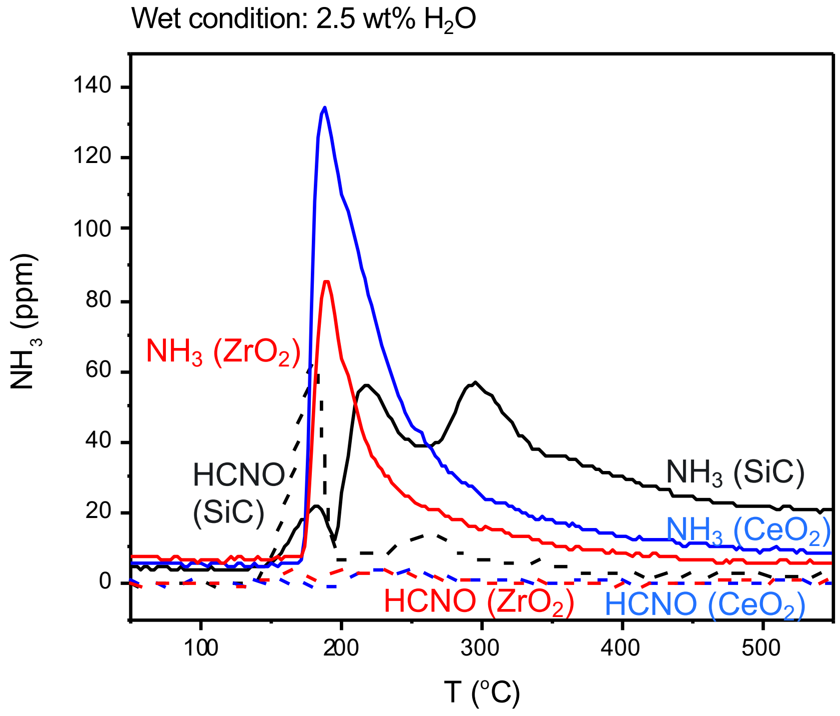
Synthesize new materials to improve existing ammonia delivery methods (USCAR and industry feedback)

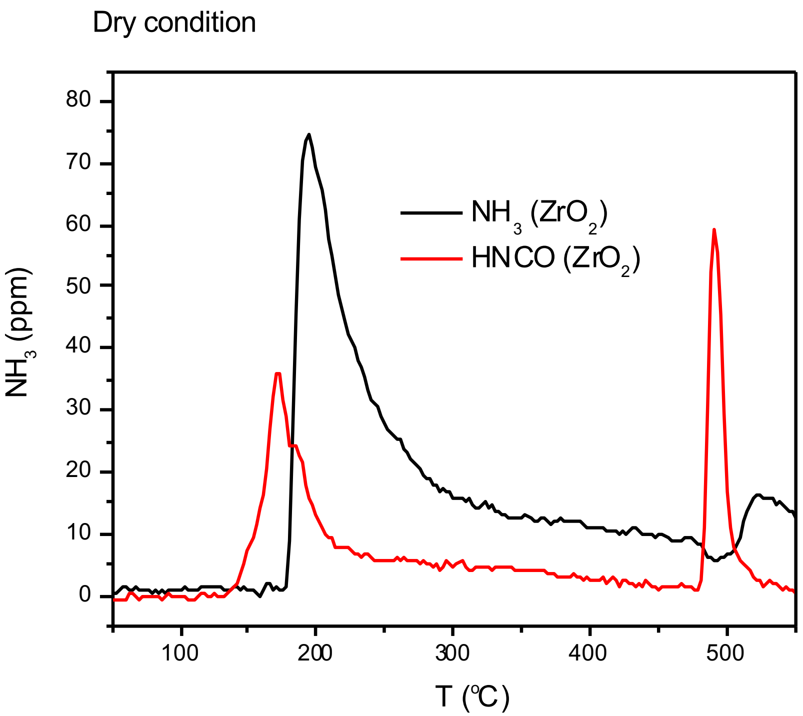
- Develop pathways to catalytic urea hydrolysis enabling NH_3 delivery at 150 °C, or
- Develop approaches to store ammonia from aqueous urea to be delivered at the currently challenging 150-180 °C temperature range

We will address difference between a proposed system compared to existing Urea/water systems, however, system investigations are beyond the scope of the current project

Isocyanic acid can be avoided with proper catalyst

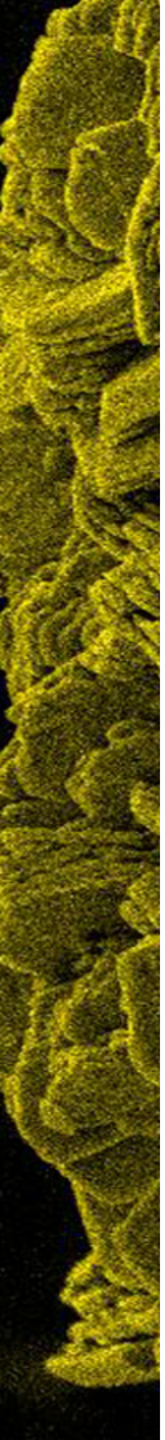






Conditions:
50 mg catalyst, 2.5 mg urea,
360 sccm N_2. 40 sccm O_2,
5 °C/min (50 to 550 °C)

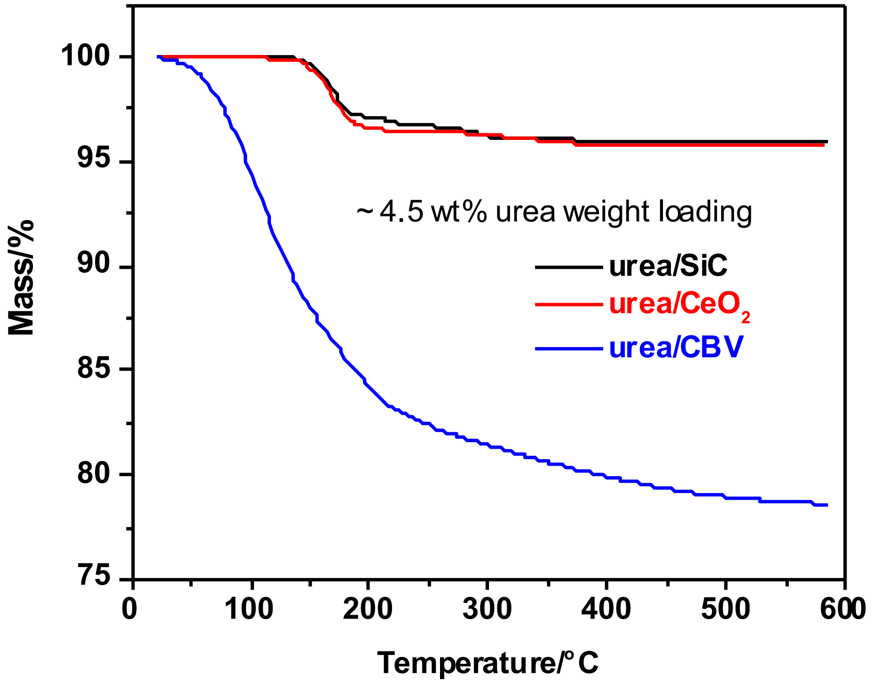
- Elimination of HCNO is key to solving onboard NH_3 storage and deposit mitigation
- Evaluating ambient condition NH_3 sorption and release

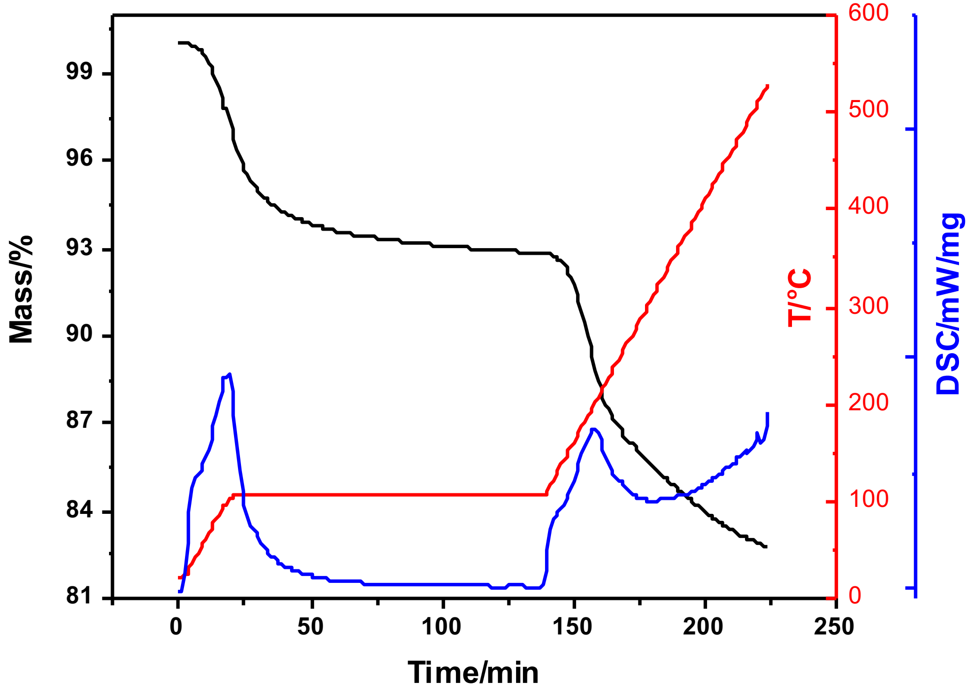


Technical Accomplishments: urea hydrolysis

Zeolite catalysts show enhanced decomposition

Differential Scanning Calorimetry Thermo Gravimetric Analysis (DSC/TGA) of urea-loaded SiC, CeO_2 and CBV





- Zeolite based catalysts show enhanced thermal decomposition of urea under dry conditions

- Zeolite-based catalysts lower the temperature of decomposition

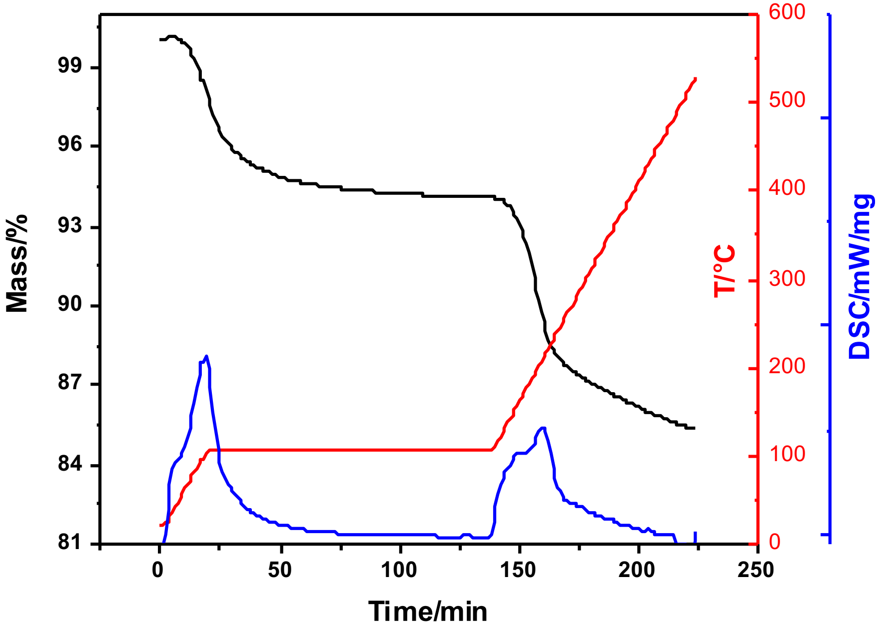
Conditions: 50 mg catalyst, 2.5 mg urea (4.75%), 5 °C/min, in N_2

Technical Accomplishments: urea hydrolysis

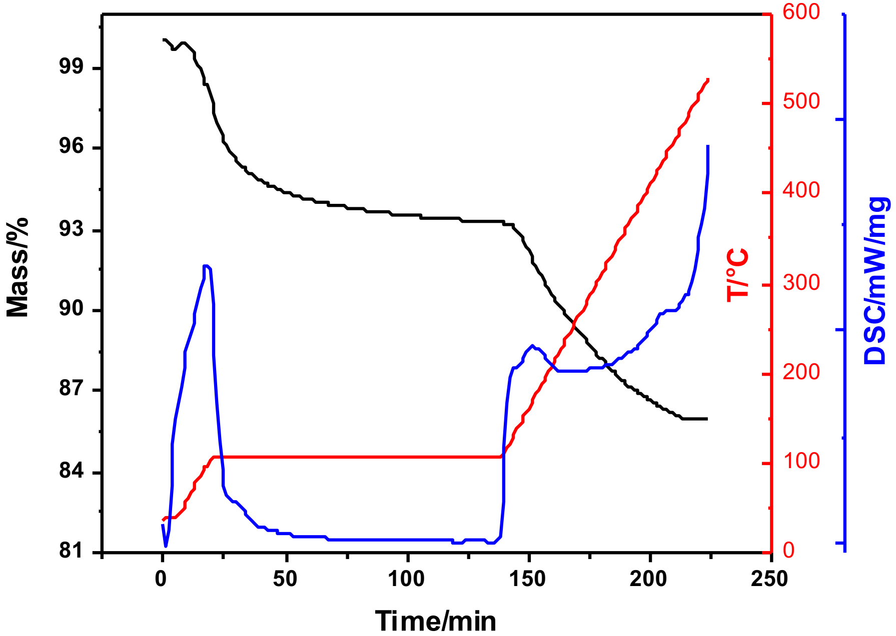
Mg zeolite is more energy efficient in extracting NH_3

DSC-TGA of urea-loaded Mg/CBV and Cu/CBV

Urea-Mg/CBV



Urea-Cu/CBV

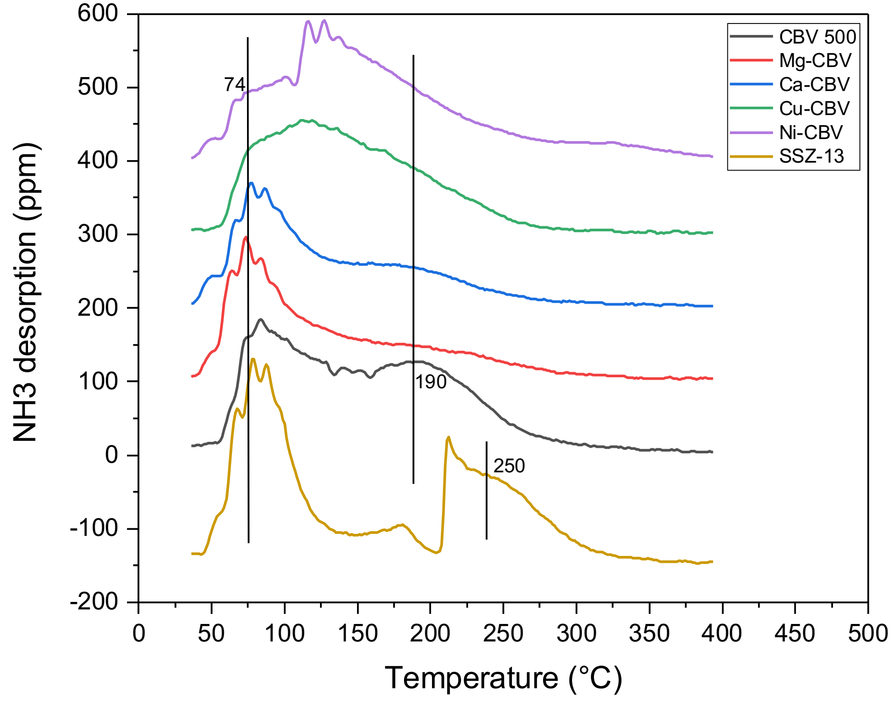


- Enthalpy of NH_3 generated from Mg exchanged zeolite is lower than that from Cu exchanged zeolite

Conditions: 50 mg catalyst, 2.5 mg urea (4.75%), 5 °C/min, in N_2

Mg and Ca addition to zeolite shifts NH_3 desorption to lower temperatures

NH_3 Temperature Programmed Desorption (TPD) Studies of Modified Zeolites



Sample	NH_3 storage (umol/g)
CBV-500	996
Mg-CBV500	688
Ca-CBV-500	652
Cu-CBV-500	773
Ni-CBV-500	913
0.05% Cu-SSZ-13	927

Amount of NH_3 adsorbed on Zeolite CBV-500 and metal modified zeolites

- Cu and Ni zeolites are not as effective as Mg and Cu
- SSZ-13 is worse than CBV 500

NH_3-TPD curves of different metal loaded CBV-500, and Cu-SSZ-13; NH_3 adsorption and purging at 35 °C prior to TPD

Conditions:
60mg catalysts, (60-80mesh); NH_3 saturated and purged at 35 °C; TPD 35 - 600 °C at 5 °C /min; N_2 = 300 cc/min

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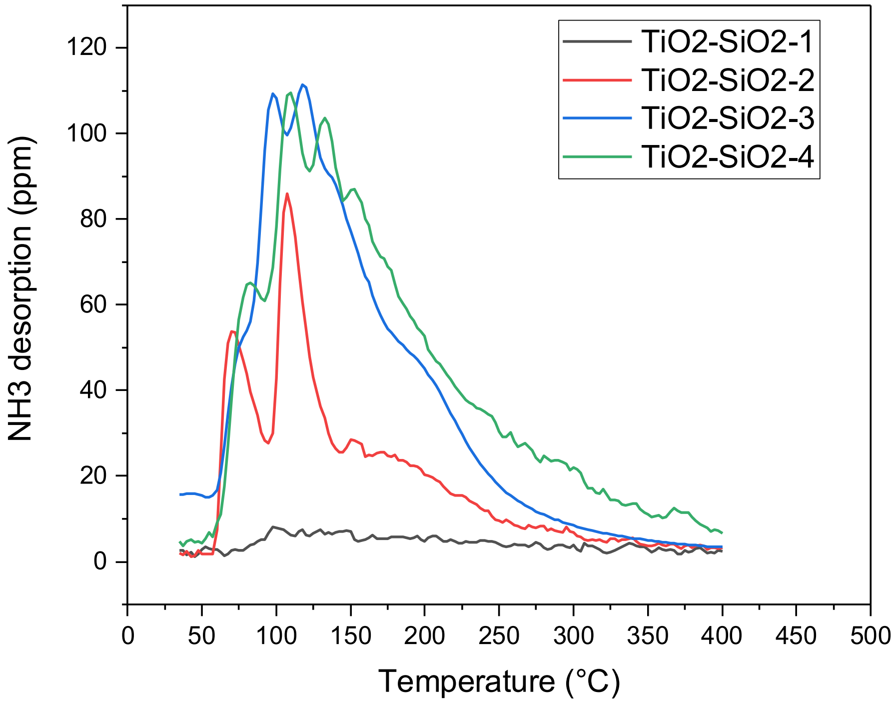
Technical Accomplishments: NH_3 storage material

TiO_2-SiO_2 releases NH_3 at lower temperature but its capacity is lower than zeolites

NH_3 Temperature Programmed Desorption (TPD) Studies of Titania Modified Silicates



Sample TiO_2-SiO_2(%)	NH_3 storage (umol/g)
1 (0%)	61.9
2(10%)	445.7
3(20%)	812.8
4(30%)	871.5

Amount of NH_3 adsorbed on TiO_2 doped SiO_2 material at different TiO_2 percentages: 0, 10%, 20%, 30%.

- TiO_2-SiO_2 materials show weaker binding of NH_3 as compared to the strongly acidic zeolites

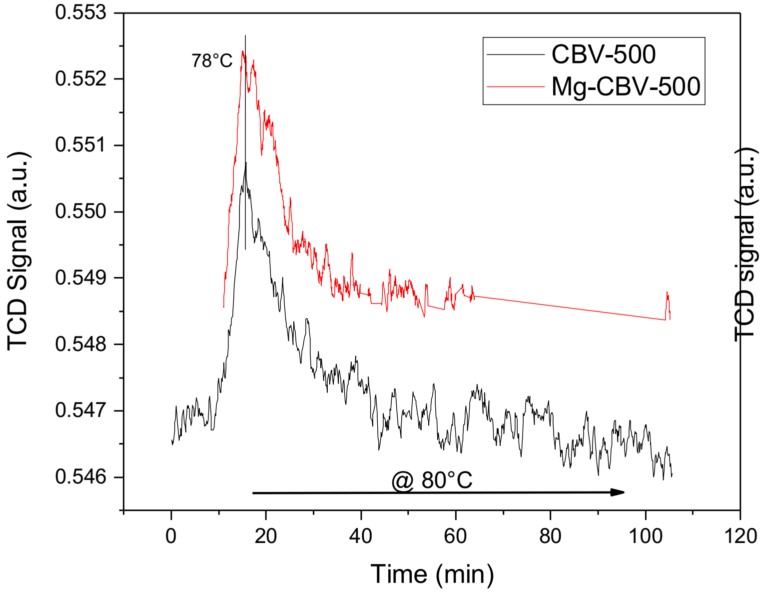
NH_3-TPD curves on TiO_2 doped SiO_2, TiO_2 percentages: 0, 10%, 20%, 30%, NH_3 adsorption and purging at 35 °C prior to TPD

Conditions:
60mg catalysts, (60-80mesh); NH_3 saturated and purged at 35 °C; TPD 35 - 600 °C at 5 °C /min; N_2 = 300 cc/min

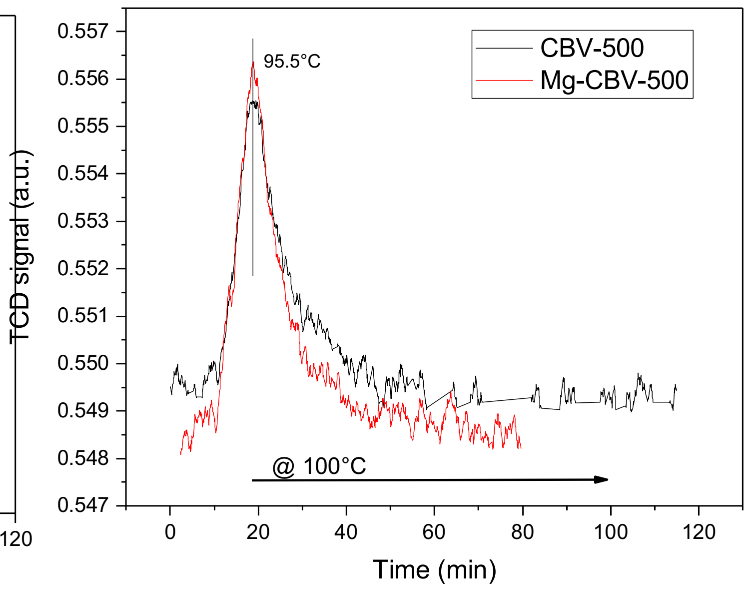
Technical Accomplishments: NH_3 storage material

Mg zeolite has no impact on low temperature release kinetics as compared to pristine zeolite

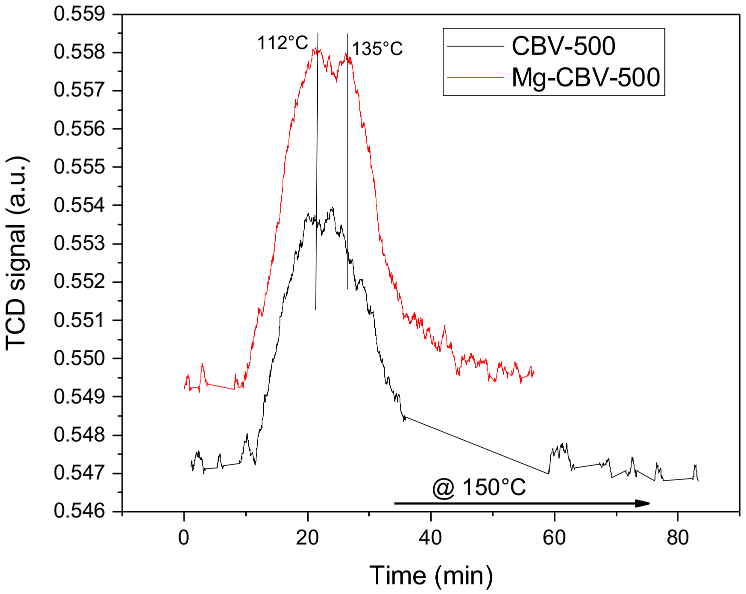
NH_3-TPD desorption curves at isothermal temperatures: 80 °C.



NH_3-TPD desorption curves at isothermal temperatures: 100 °C.



NH_3-TPD desorption curves at isothermal temperatures: 150 °C.



- Studies on other ion-exchanged zeolites underway

Conditions:
60mg catalysts, (60-80mesh); NH_3 saturated and purged at 35 °C; TPD 35 - 600 °C at 5 °C /min; N_2 = 300 cc/min

Responses to Previous Year Reviewers' Comments

Reviewers' Comments	PNNL Responses
Is gaseous ammonia delivery the right path forward for low-temperature NOx abatement given the market share of Amminex or similar technologies and the existing infrastructure for DEF/urea water solution.	We are working on evaluating ammonia storage from urea/water system which can enable low temperature dosing in two regimes: • 150-180 °C where urea/water is not feasible, but SCR catalysts are functional • <150 °C for low temperature SCR activity in future • We are evaluating catalytic hydrolysis of urea
Solid sorbents have been around for a while now. Consulting with the industry for advice on what materials have already been studied and what needs to be avoided so as not to repeat prior work	We are consulting with additional industrial contacts for advice including engine companies, heavy duty and light duty manufacturers
That it would be very useful to put the results generated so far into context by comparison with the current state of the art. The NH_3 adsorption studies on various materials are difficult to judge unless compared to the targets set by commercial applications (such as how much NH_3 is needed over a drive cycle or through urea delivery via DEF today.	See table

	USCAR FTP cycle
Total NH3	4.8 g
Avg. mass flow	3.1 mg/s
Peal flow	22.6 mg/s
Cycle length	1399 sec

Collaborations/ Interactions

OEM
Development Teams and Suppliers

Project Management PNNL

USCAR

Provide results of current performance metrics of various NH_3 storage materials and feedback on material performance

PNNL

Carry out and disseminate results of synthesis, characterization, testing and provide recommenda-tions to USCAR

DOE EERE Vehicle Technologies Program

Gurpreet Singh, Ken Howden, Siddiq Khan

Collaborators/ Coordination

- USCAR/SCR working group
- Cummins: Consulting
- Future: PACCAR, Faurecia, Umicore

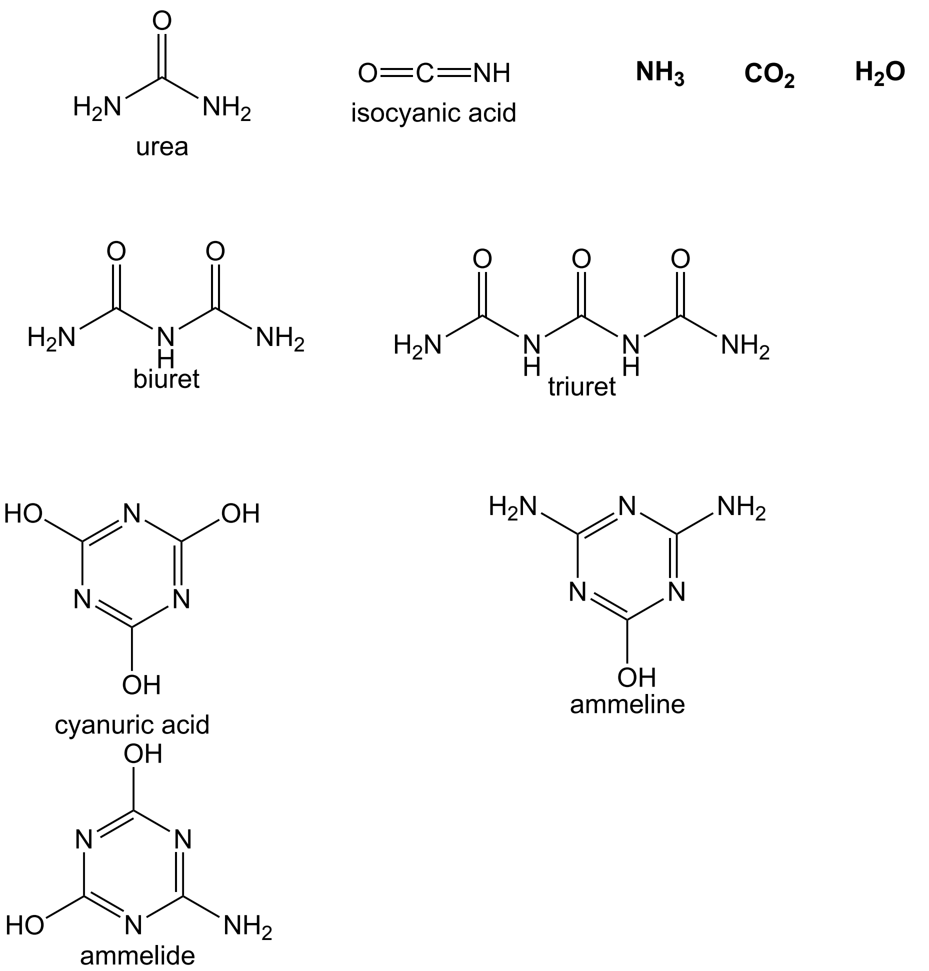
Communication plan

- Monthly updates and teleconference with USCAR PI
- Bi-annual face-to-face meeting with USCAR SCR team

Remaining Challenges and Barriers

- Mechanistic understanding of mitigation of isocyanic acid byproducts such as biuret and ammelide
- Understanding the impact of metal ion loading on ammonia storage and release
- Impact of water and CO_2 on NH_3 storage and release.

Urea hydrolysis intermediates with isocyanic acid



A.M. Bernhard et al. / Applied Catalysis B: Environmental 115–116 (2012) 129–137

Proposed Future Work

- Evaluate catalytic urea hydrolysis performances at temperatures between 130-180 °C
- Determine pathways to mitigate HCNO and biurets formation
- Modification of zeolites to enhance ammonia storage capacity and release kinetics
- Study the effect of water and CO_2 on ammonia storage capacity

Any proposed future work is subject to change based on funding levels

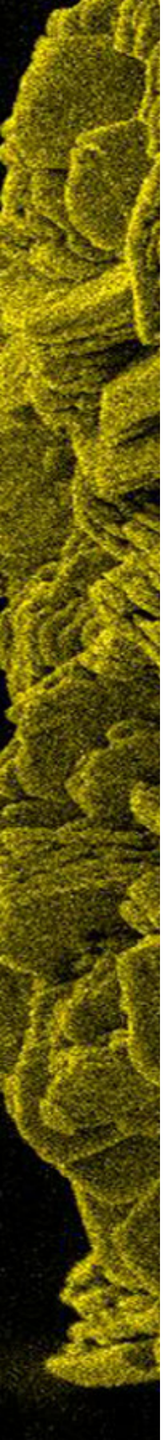
Summary

Urea hydrolysis

- Completed initial evaluation of catalytic urea hydrolysis
  - Preliminary studies show decreased formation of isocyanic acid during catalytic hydrolysis
  - Metal oxide (CeO_2 and ZrO_2) show no isocyanic acid formation
  - No decrease in temperature of urea hydrolysis

NH_3 storage material

- Ion exchanged zeolite materials provide ability to tune temperature of NH_3 delivery
  - Mg and Ca exchanged zeolite show lower capacity and temperature for NH_3 release
  - TiO_2-SiO_2 materials show weaker binding of NH_3 as compared to zeolites



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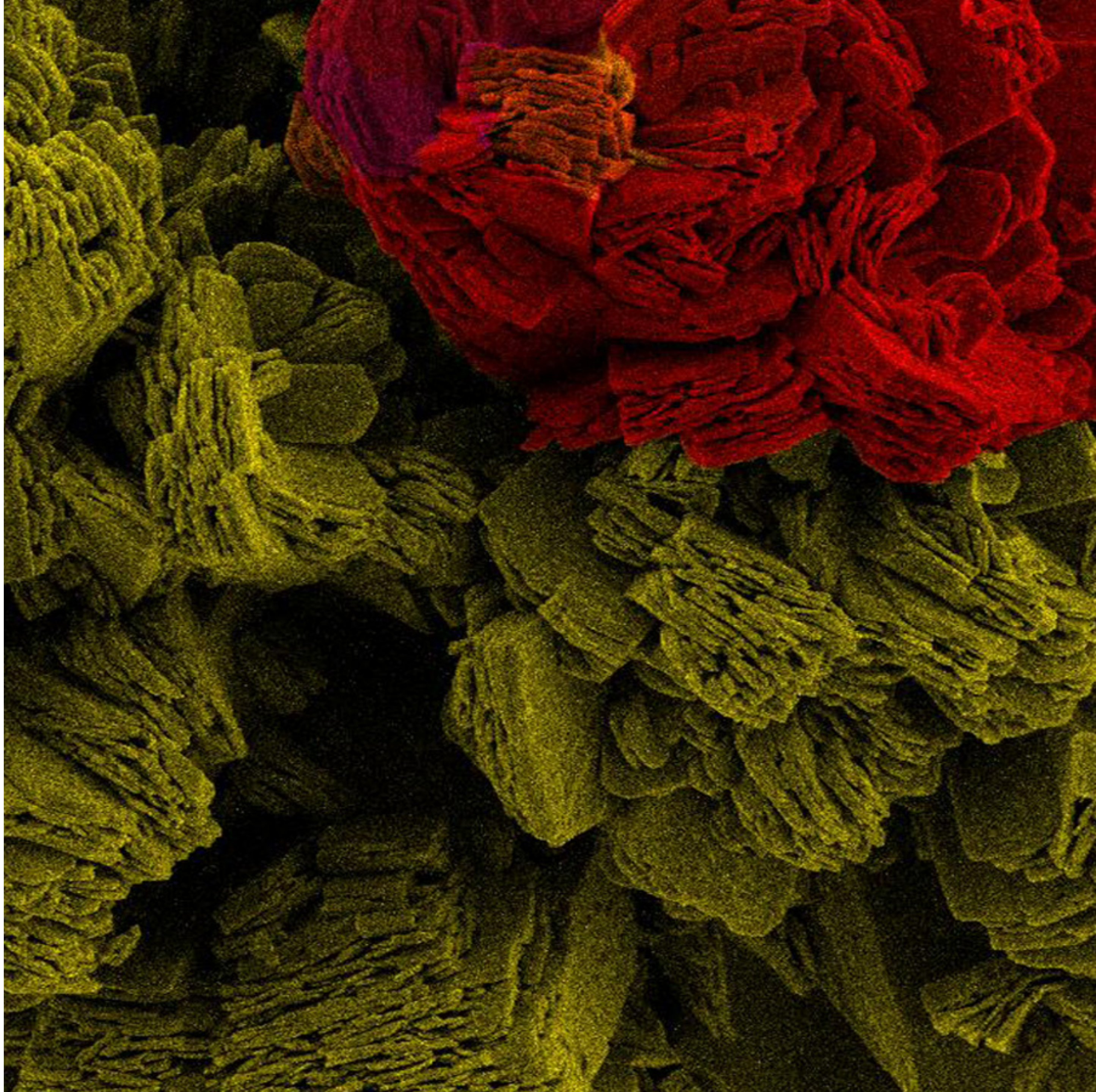
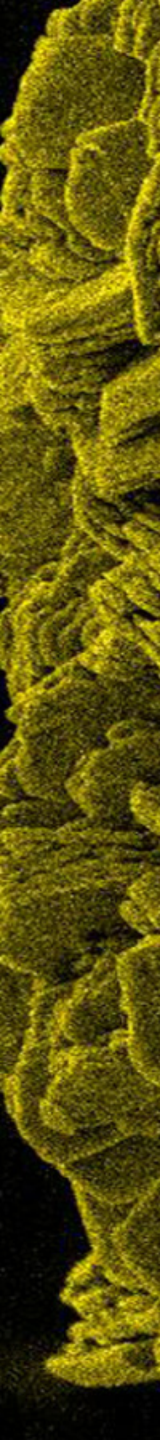
Thank you





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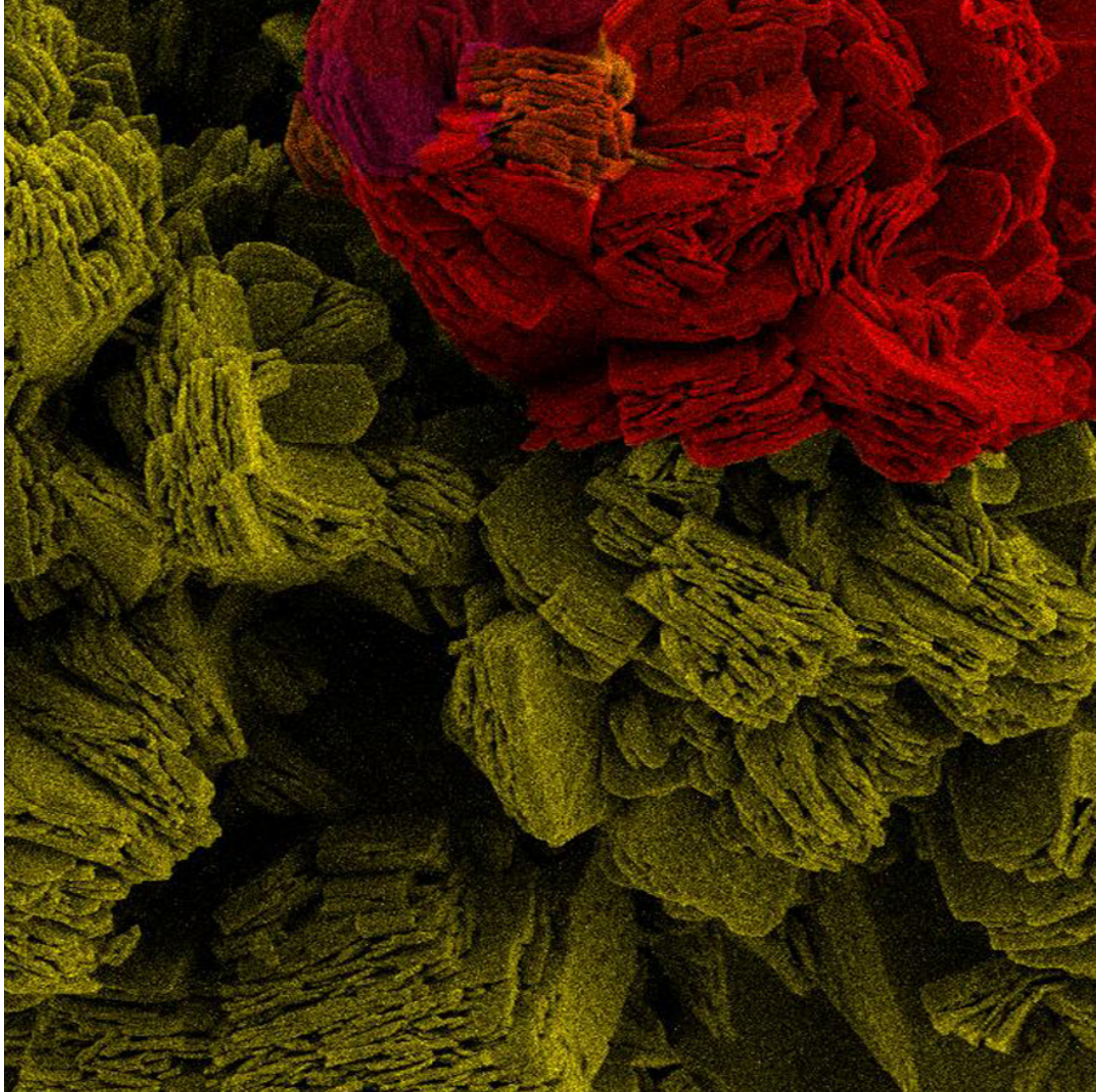
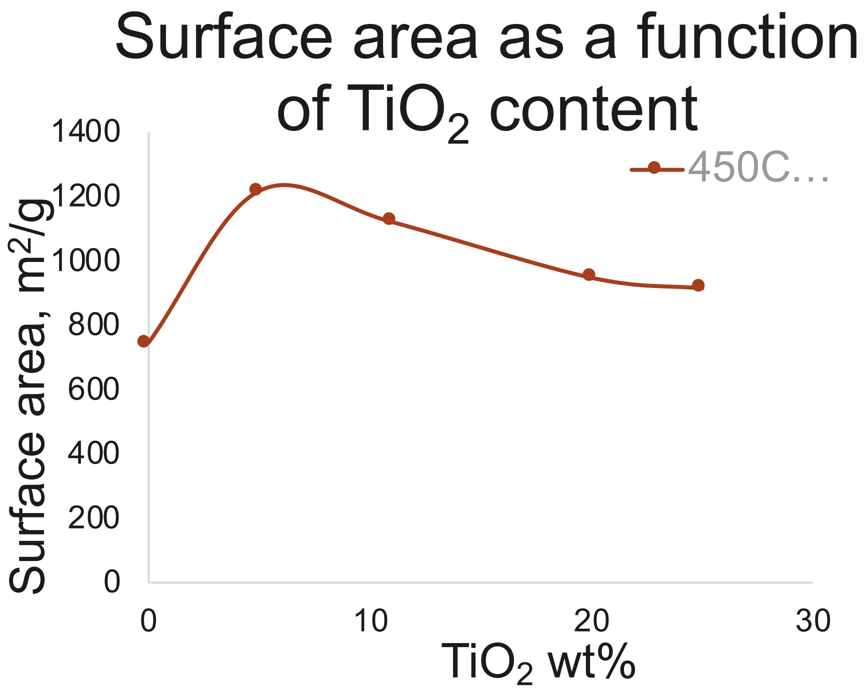
Technical Backup Slides

VTO AMR June 1-4, 2020



Surface area as a function of TiO2 content and calcination temperature

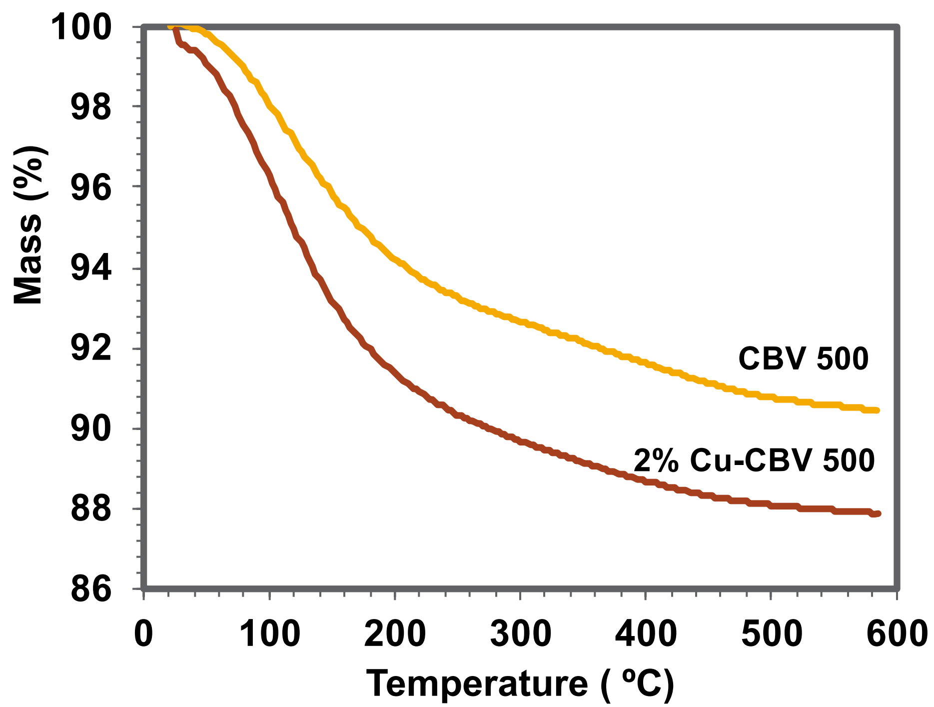


TiO_2 wt%	Calcination temperature, ^oC	Surface area, m^2/g	pore size, A
0	450	746	17
0	550	649	
5	450	1217	20
5	550	1082	
11	450	1120	24
11	550	1013	
20	450	947	27
20	550	911	
25	450	914	30
25	550	705	

The surface area decreases as the calcination temperature increases. Addition of TiO_2 to SiO_2 not only increases the surface area but also improves the thermal stability of the material.

Screening of NH_3 adsorption on porous materials

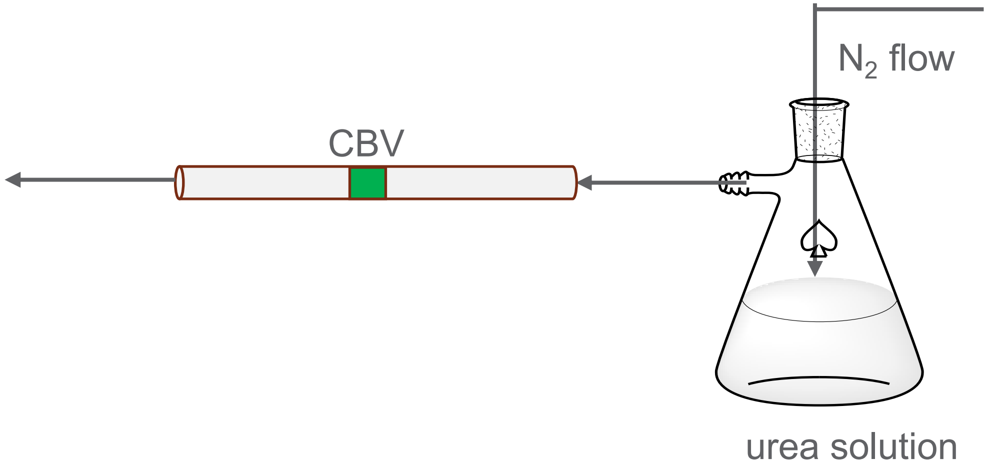
Differential Scanning Calorimetry Thermo Gravimetric Analysis (DSC/TGA) of NH3-loaded CBV



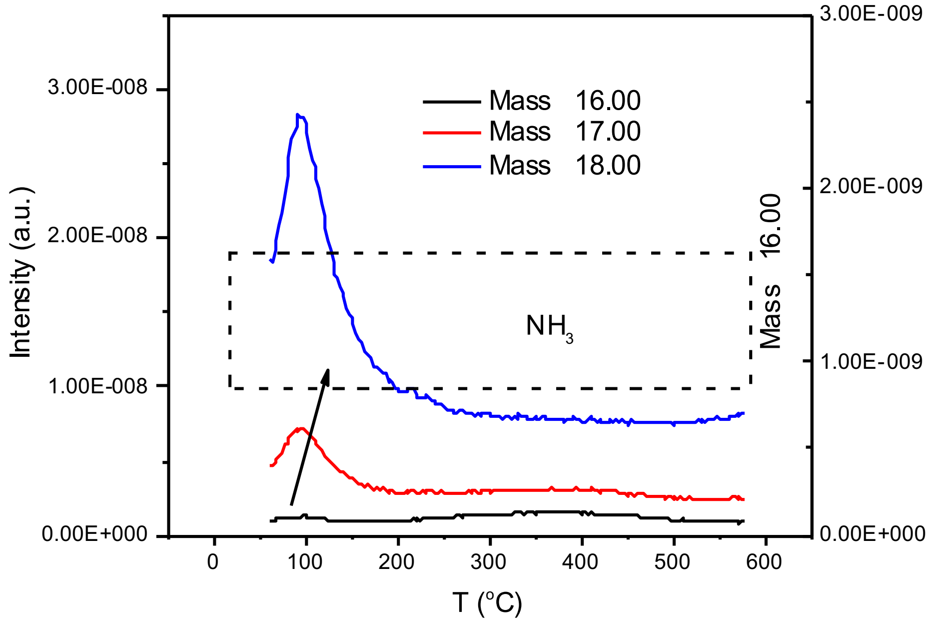
Materials	NH_3 capacity (Wt%)	Impregnation method
MCM-41	4.55	
Al-MCM-41	5.55	Incipient wetness
Zeolite Y CBV500	9.55	
2%Cu_zeolite Y CBV500	12.13	Incipient wetness
Ca_zeolite Y CBV 500	16.68	Ion-exchange
Montmorillonite_AR	3.62	
Cu_montmorillonite	7.10	Ion-exchange

- We screened several classes of oxide based materials for NH_3 uptake and release

Flow-through Urea decomposition studies



Dry at 80 °C overnight before test



30 °C, 24 h